Synthesis of Functionalized Olefins *via* Cross and Ring-Closing Metatheses

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Supporting Material

Experimental procedures and characterization (^{1}H and ^{13}C NMR, HRMS/elemental analysis, FTIR) employed in the preparation of cross and ring-closing metathesis products. ^{1}H NMR spectra for 3, 15, 16, 17, 18, 22, 23, 24 (8 pages). ^{13}C NMR spectra for 15, 16, 17, 18 (4 pages), ^{31}P NMR spectra for 3 (1 page).

General Experimental Section. NMR spectra were recorded on either a JEOL GX-400 or GE-300 NMR. Chemical shifts are reported in parts per million

(ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and multiplet (m). The reported ^{1}H NMR data refer to the major olefin isomer unless stated otherwise. The reported ^{13}C NMR data include all peaks observed and no peak assignments were made. High-resolution mass spectra (EI and FAB) were provided by the UCLA Mass Spectrometry Facility (University of California, Los Angeles).

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. All other chemicals were purchased from the Aldrich, Strem, or Nova Biochem Chemical Companies, and used as delivered unless noted otherwise. CH_2Cl_2 was purified by passage through a solvent column prior to use.[i]

NMR scale experiments were performed in J. Young valve NMR tubes under an N_2 atmosphere with 20 equivalents of functionalized olefin to 1 equivalent of catalyst **3** in CD_2Cl_2.

Compound 3. A 250-mL flame-dried round bottom flask equipped with a magnetic stirbar was charged with 1,3-dimesityl-4,5-dihydro-imidazolium tetrafluoroborate (3.08 g, 7.80 mmol, 1.6 equiv.) and dry THF (30 mL) under nitrogen atmosphere. A solution of potassium *tert*-butoxide (0.88 g, 7.80 mmol, 1.6 equiv.) in dry THF (30 mL) was slowly added at room temperature. The reaction mixture was allowed to stir for 1/2 hour and was then slowly transferred to a 500-mL flame-dried Schlenk flask containing a solution of $RuCl_2(=CH=C(CH_3)_2)(PCp_3)_2$ (3.50 g, 4.88 mmol, 1.0 equiv.) in dry toluene (200 mL). This mixture was stirred at 80°C for 15 min, at which point

the reaction was complete as indicated by ^{1}H NMR. The reaction mixture was filtered through a glass frit under argon and all volatiles were removed under high vacuum. The residue was recrystallized three times from anhydrous methanol (40 mL) at –78°C to give **3** as a pinkish-brown microcrystalline solid (2.95 g) in 77% yield: ^{1}H NMR (C_6H_6, 400 MHz) δ 19.16 (d, J = 11 Hz, 1H), 7.71 (d, J = 11 Hz, 1H), 6.89 (s, 2H), 6.62 (s, 2H), 3.36-3.24 (m, 4H), 2.80 (s, 6H), 2.54 (s, 6H), 2.41-1.26 (br m, 27H), 2.20 (s, 3H), 2.02 (s, 3H), 1.06 (s, 3H), 0.90 (s, 3H); ^{31}P NMR (C_6H_6, 161.9 MHz) δ 28.05; HRMS (FAB) $C_{41}H_{61}Cl_2N_2PRu$ [M^+] 784.2993, found 784.2963.

Reaction of Compound 3 with ethyl vinyl ether. After 8 hours at 45°C, catalyst **3** is only partially converted to a new Fischer carbene species. The new carbene species has the following characteristic resonances (CD_2Cl_2): ^{1}H NMR: 13.6 ppm; ^{31}P NMR: 27.3 ppm. Some additional uncharacterized phosphine-containing products were observed by ^{31}P NMR during the course of the reaction.

Compound 13. 9-Decen-1(*tert*-butyldimethylsilane)-yl (330 μL, 1.0 mmol) and Methyl methacrylate (55 μl, 0.51 mmol) were added simultaneously *via* syringe to a stirring solution of **3** (21 mg, 0.026 mmol, 5.2 mol %) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A viscous oil was obtained (110 mg, 62% yield, *trans/cis* as determined by relative heights at 143.2 and 143.1 ppm of ^{13}C NMR spectra). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.75 (1H, m), 3.71 (3H, s), 3.57 (2H, t, J = 6.3 Hz), 2.14 (2H, m), 1.81 (3H, app s), 1.50 – 1.05 (12H, broad m), 0.87 (9H, s), 0.02 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 169.2,

143.2, 143.1, 128.0, 63.8, 52.1, 33.4, 30.0, 29.8, 29.2, 29.1, 26.5, 26.3, 18.9. 12.9. R_f = 0.81 (9:1 hexane:ethyl acetate); HRMS (EI) calcd for $C_{19}H_{38}O_3Si$ [M+ H]$^+$ 343.2668, found 343.2677. Elemental analysis Calcd: C: 66.61, H: 11.18; Found: C: 66.47, H: 11.03.

Compound 14. 9-Decen-1-yl benzoate (145 µl, 0.52 mmol) and Methyl acrylate (90 µl, 1.0 mmol) were added simultaneously *via* syringe to a stirring solution of **3** (17 mg, 0.022 mmol, 4.2 mol %) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A white crystalline solid was obtained (151.4 mg, 91% yield, 4.5:1 *trans/cis* as determined by relative integrations of ^{1}H peaks at 3.75 and 3.68 ppm). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.01 (2H, app d, J = 7.2 Hz), 7.50 (1H, m), 7.45 (2H, m), 6.93 (1H, dt, J = 15.9 Hz, 6.9 Hz), 5.78 (1H, app d, J = 15.9 Hz), 4.28 (2H, t, J= 6.6 Hz), 3.68 (3H, s), 2.15 (2H, m), 1.74 (2H, p, J = 6.6 Hz), 1.49 – 1.05 (10H, broad m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 167.5, 167.1, 150.0, 133.3, 131.1, 130.0, 128.8, 121.5, 65.5, 51.8, 32.7, 29.8, 29.5, 29.2, 28.5, 26.5. R_f = 0.40 (9:1 hexane:ethyl acetate); HRMS (EI) calcd for $C_{19}H_{26}O_4$ [M+ H]$^+$ 319.1909, found 319.1914. Elemental analysis Calcd: C: 71.67, H: 8.23; Found: C: 71.31, H: 8.24.

Compound 15. A flame-dried round-bottomed flask equipped with reflux condenser was charged with 5-acetoxy-1-hexene (184 mg, 1.3 mmol, 2.5 eq.), methacrolein (35 mg, 0.5 mmol, 1.0 eq.), and dichloromethane (2.5 mL). Catalyst **3** (20 mg, 25 µmol, 0.05 eq.) was subsequently added as a solid, producing a light brown solution which

was refluxed for 12 hours. The mixture was then concentrated *in vacuo* to a dark brown oil. Purification of this residue by silica gel chromatography (8:2 hexanes:ethyl acetate) allows isolation of 85 mg (0.46 mmol, 92%) of a clear oil (R_f = 0.44). This compound darkens rapidly (under one hour) in air at room temperature and/or in the presence of light, resulting in isomerization and production of uncharacterized polar side products. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.34 (1H, s), 6.43 (1H, t, J = 5.5 Hz), 4.02 (2H, t, J = 5.0 Hz), 2.34 (2H, t, J = 5.5 Hz), 1.99 (3H, s), 1.68 (3H, s), 1.65-1.50 (4 H, m). HRMS (EI) calcd. for $C_{10}H_{16}O_3$ $[M]^+$ 184.1099, found 184.1094.

Compound 16. A flame-dried round-bottomed flask equipped with reflux condenser was charged with 5-acetoxy-1-hexene (71 mg, 0.5 mmol, 1.0 eq.), acrolein (73 mt, 1.3 mmol, 2.6 eq.), and dichloromethane (2.5 mL). Catalyst **3** (20 mg, 25 μmol, 0.05 eq.) was subsequently added as a solid, producing a light brown solution which was refluxed for 12 hours. The mixture was then concentrated *in vacuo* to a dark brown oil. Purification of this residue by silica gel chromatography (9:1 hexanes:ethyl acetate) allows isolation of 52 mg (0.3 mmol, 62%) of a clear, colorless oil (R_f = 0.23). The title compound is produced as a mixture of isomers, *trans:cis* = 1.1:1 determined by integration of peaks at 9.50, 9.47, 7.03 and 6.83 ppm ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.50 (1H, s), 9.47 (1H, s), 7.03 (1H, dt, J = 7.1, 18 Hz), 6.83 (1H, dt, J = 6.8, 15.6 Hz), 6.1 (1H, qt, J = 1.5, 8.1 Hz), 5.82 (1H, dt, J = 1.5, 15.6 Hz), 4.05 (2H, dt, J = 4.5, 6.3 Hz), 2.38 (2H, q, J = 6.9 Hz), 2.24 (2H, q, J = 6.9 Hz), 2.03 (3H, s), 1.69-1.52 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 194.0, 171.2, 157.9, 151.1, 133.2, 121.0, 63.9, 32.1, 31.7, 28.0, 24.2, 22.6, 20.9, 14.0. HRMS (EI) calcd. for $C_9H_{14}O_3$ $[M]^+$ 170.0943, found 170.0878.

Compound 17. A flame-dried round-bottomed flask equipped with reflux condenser was charged with 5-acetoxy-1-hexene (32 mg, 0.2 mmol, 1.0 eq.), phenyl vinyl ketone (60 mg, 0.5 mmol, 2.5 eq.), and dichloromethane (1 mL). Catalyst **3** (7 mg, 8 μmol, 0.04 eq.) was subsequently added as a solid, producing a light brown solution which was refluxed for 12 hours. The mixture was then concentrated *in vacuo* to a dark brown oil. Purification of this residue by silica gel chromatography (7:3 hexanes:ethyl acetate) allows isolation of 49 mg (0.2 mmol, 99%) of a thin, clear yellow oil ($R_f = 0.54$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.85 (1H, dd, J = 1.2, 6.9 Hz), 7.48 (2H, tt, J = 1.2, 7.2 Hz), 7.39 (2H, t, J = 7.5 Hz), 7.00 (1H, dt, J = 7.6, 15 Hz, *trans* isomer), 6.83 (1H, dt, J = 1.1, 15.6 Hz), 4.01 (2H, t, J = 6.3 Hz), 2.28 (2H, q, J = 6.9 Hz), 1.97 (3H, s), 1.64-1.49 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 190.4, 170.8, 148.6, 137.7, 132.4, 128.3, 126.1, 108.5, 63.8, 32.0, 27.9, 24.4, 20.6. HRMS (EI) calcd. For $C_{15}H_{18}O_3$ $[M]^+$ 246.1256, found 246.1255.

Compound 18. A flame-dried round-bottomed flask equipped with reflux condenser was charged with 5-acetoxy-1-hexene (71 mg, 0.5 mmol, 1.0 eq.), methyl vinyl ketone (91 mg, 1.3 mmol, 2.2 eq.), and dichloromethane (2.5 mL). Catalyst **3** (20 mg, 25 μmol, 0.05 eq.) was subsequently added as a solid, producing a light brown solution which was refluxed for 12 hours. The mixture was then concentrated *in vacuo* to a dark brown oil. Purification of this residue by silica gel chromatography (7:3 hexanes:ethyl acetate) allows isolation of 87 mg (0.47 mmol, 95%) of a clear, colorless oil ($R_f = 0.33$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.68 (1H, dt, J = 6.9, 15.9 Hz), 5.97 (1H, dt, J = 1.5, 6 Hz), 3.96 (2 H, t, J = 6.6 Hz), 2.17 (2H, pentet, J = 1.5 Hz), 2.13 (3 H, s), 1.93 (3 H, s), 1.55-1.44 (4 H, broad multiplet). ^{13}C NMR (75

MHz, $CDCl_3$, ppm): δ 198.2, 170.8, 147.3, 131.3, 63.7, 31.7, 27.9, 26.6, 24.2, 22.4, 20.7. HRMS (EI) calcd. For $C_{10}H_{16}O_3$ $[M]^+$ 184.1099, found 184.1099.

Compound 22. 9-Decen-1-yl benzoate (145 μl, 0.52 mmol) and butadiene monoxide (160 μl, 1.98 mmol) and was added simultaneously *via* syringe to a stirring solution of **3** (21 mg, 0.027 mmol, 5.0 mol %) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 20:1 hexane:ethyl acetate. A clear oil was obtained (95 mg, 55% yield, 5:1 *trans/cis* as determined by relative integrations of ^1H peaks at 5.94 and 5.75 ppm). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.03 (2H, app d, J = 7.2 Hz), 7.55 (1H, m), 7.44 (2H, m), 5.94 (1H, dt, J = 15.3 Hz, 6.9 Hz), 5.12 (1H, dd, J = 8.7 Hz, 6.3 Hz), 4.31 (2H, t, J= 6.6 Hz), 3.30 (1H, m), 2.63 (1H, m), 2.03 (1H, m) 1.76 (2H, m), 1.51-1.22 (10H, broad m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 167.2, 137.8, 137.6, 133.3, 130.1, 128.9, 128.1, 65.6, 53.0, 49.3, 32.9, 29.9, 29.7, 29.6, 29.4, 29.3, 26.6. R_f = 0.38 (9:1 hexane:ethyl acetate); HRMS (EI) calcd for $C_{19}H_{26}O_3$ $[M+ H]^+$ 303.1960, found 303.1960.

Compound 23. 2,2,3,3,4,4,5,5,6,6,6-Nonaflouro-1-hexene (175 μl, 1.0 mmol) and 5-Hexenyl-1-acetate (85 μl, 0.51 mmol) were added simultaneously *via* syringe to a stirring solution of **3** (17 mg, 0.022 mmol, 4.2 mol %) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. An amber oil was obtained (62 mg, 34% yield, 2.3:1 *trans/cis* as determined by relative intensities of ^{13}C peaks at

143.0 and 143.2 ppm). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 6.40 (1H, m), 5.65 (1H, m), 4.07 (2H, t, J = 6.3 Hz), 2.10 (2H, m), 2.05 (3H, app s), 1.72 (2H, m), 1.53 (2H, m) ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 171.6, 143.2, 143.0, 118.2, 117.8, 117.5, 64.5, 32.1, 32.0, 28.5, 25.0, 23.2, 21.4, 14.6. R_f = 0.72 (9:1 hexane:ethyl acetate).

Compound 24. Vinyltriethoxysilane (190 µl, 1.0 mmol) and 5-Hexenyl-1-acetate (85 µl, 0.51 mmol) were added simultaneously *via* syringe to a stirring solution of **3** (21 mg, 0.027 mmol, 5.2 mol %) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 10:1 hexane:ethyl acetate. A clear oil was obtained (126 mg, 81% yield, 11:1 *trans/cis* as determined by integration of ^{1}H NMR peaks at 5.40 and 5.28 ppm). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.38 (1H, dt, J = 18.9 Hz, 6.3 Hz), 5.41 (1H, app d, J = 18.9 Hz), 4.03 (2H, t, J = 6.3 Hz), 3.79 (6H, q, 6.9 Hz), 2.16 (2H, m), 2.02 (3H, s), 1.59 (2H, m), 1.47 (m, 2H), 1.20 (9H, t, J = 7.1 Hz. ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.6, 153.4, 120.3, 64.8, 64.4, 58.9, 58.8, 36.5, 36.3, 28.8, 28.6, 25.2, 24.4, 18.7. R_f = 0.31 (10:1 hexane:ethyl acetate). HRMS (FAB) calcd for $C_{14}H_{28}O_5Si$ $[M+H]^+$ 305.1784, found 305.1770.

Compound 31. A 250 mL oven-dried round bottom flask equipped with a stir bar was charged with CH_2Cl_2 (156 mL), **25** (1.00 g, 7.80 mmol, 1 equiv.) and **3** (331 mg, 0.42 mmol, 0.05 equiv.). The reaction mixture was refluxed overnight, at which time the ^{1}H NMR indicated complete disappearance of the starting material. CH_2Cl_2 was distilled off at ambient pressure and the product was purified by bulb-to-bulb distillation to yield **30** as a colorless oil (382 mg, 3.78 mmol, 49% yield).

Characterization by: Bottini, A. T.; Corson, F. P.; Bottner, E. F. *J. Org. Chem.* **1965**, *30*, 2988-2994.

Compound 33. Compound **27** (35 μl, 0.25 mmol) was added *via* syringe to a stirring solution of **3** (11 mg, 0.022 mmol, 5.6 mol %) in CH_2Cl_2 (12.5 ml, 0.02 M). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate (R_f= 0.25). A clear oil of **32** was obtained (27 mg, 97% yield). Characterization by: Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. *Tetrahedron Lett.* **1990**, *31*, 197-200.

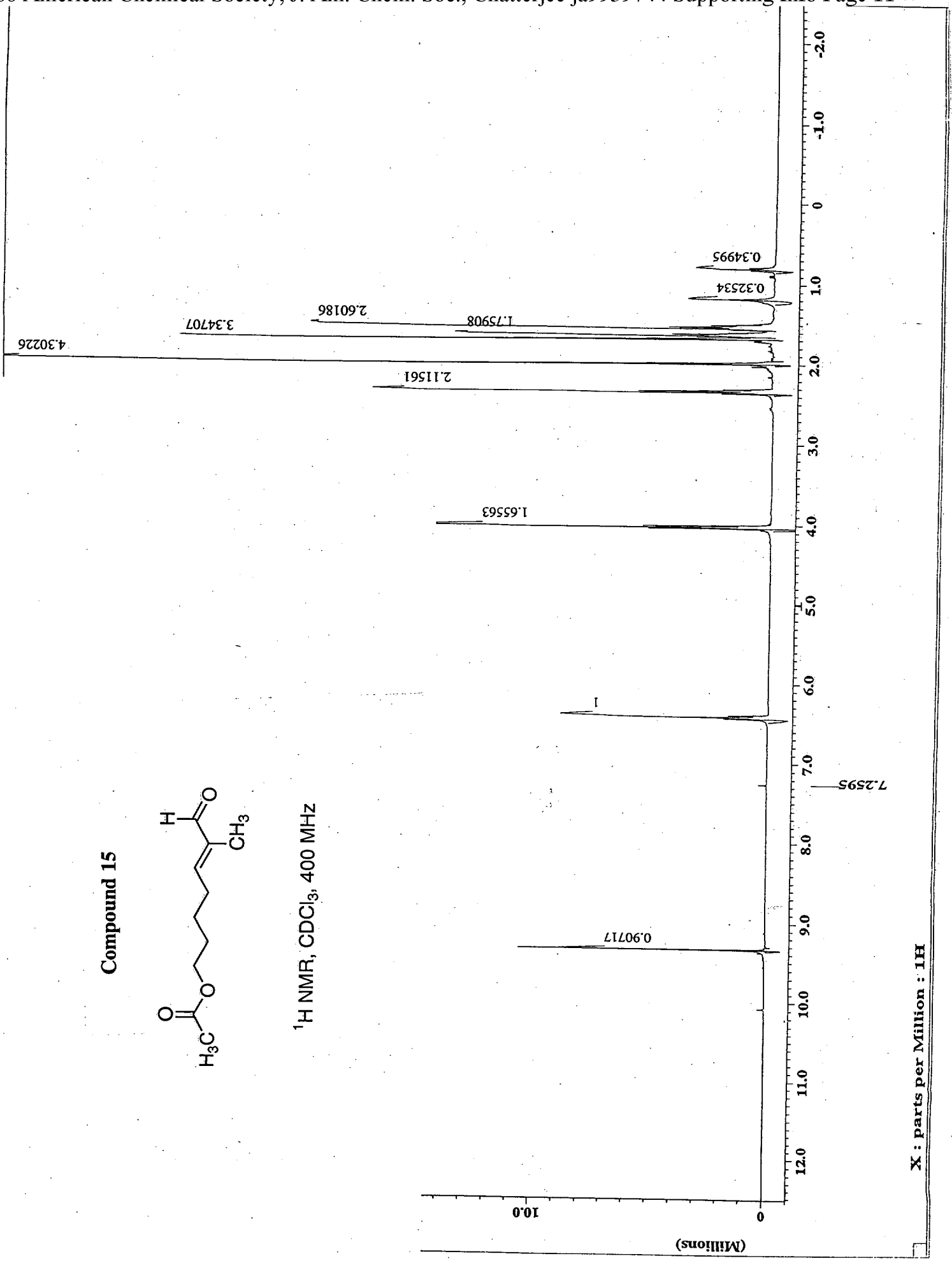
Compound 34. Compound **28** (40 μl, 0.26 mmol) was added *via* syringe to a stirring solution of **3** (9.8 mg, 0.013 mmol, 4.8 mol %) in CH_2Cl_2 (12.5 ml, 0.02 M). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate (R_f= 0.25). A clear oil of **33** was obtained (30 mg, 92% yield). Characterization by: Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. *Tetrahedron Lett.* **1990**, *31*, 197-200.

Compound 35. Compound **29** (70 μl, 0.51 mmol) was added *via* syringe to a stirring solution of **3** (18 mg, 0.023 mmol, 4.5 mol %) in CH_2Cl_2 (10 ml, 0.05 M). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate (R_f = 0.45). A clear oil of **34**

was obtained (30 mg, 92% yield). Characterization by: Dupont, J.; Donato, A. J. *Tetrahedron: Asymm.* **1998**, *9*, 949-954.

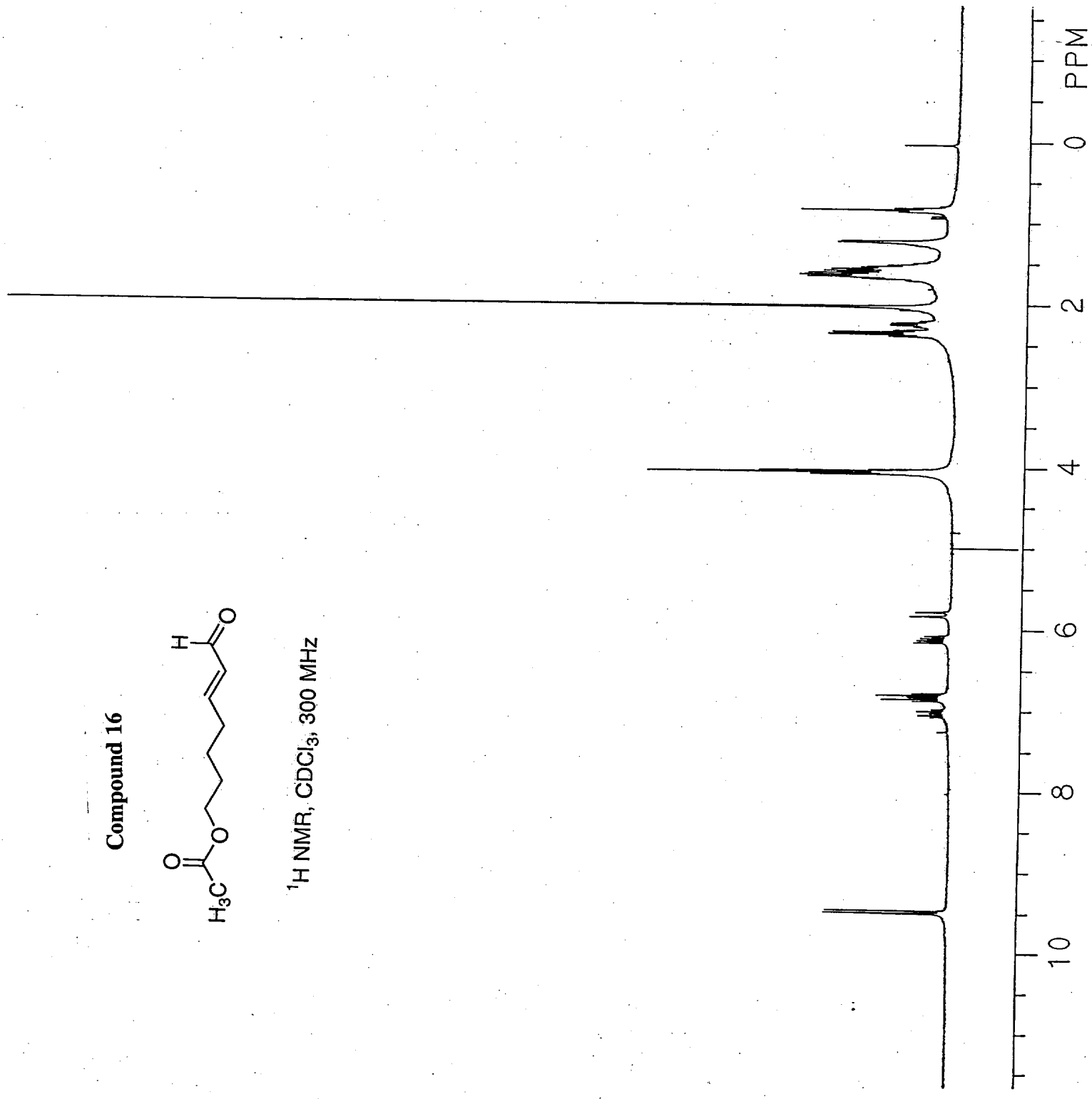
Compound 36.. Compound **30** (0.11 g, 0.18 mL, 1.0 mmol) was added via syringe to a homogenous, stirred solution of **3** (41 mg, 0.052 mmol, 5.2 mol. %) in CH_2Cl_2 (50 mL, 0.02 M). The resultant dark brown solution was refluxed under a nitrogen stream for 12 hours. The reaction mixture was then concentrated *in vacuo* and purified by silica gel column chromatography (6:4 ethyl acetate:hexanes, $R_f = 0.55$). The product, Cyclopent-2-en-1-one, was isolated as a clear oil in 93% yield (81 mg, 0.98 mmol) which is identical in all respects to an authentic sample obtained from Aldrich Chemicals.

(i) The solvent columns are composed of activated alumina (A-2) and supported copper redox catalyst (Q-5 reactant). See: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.



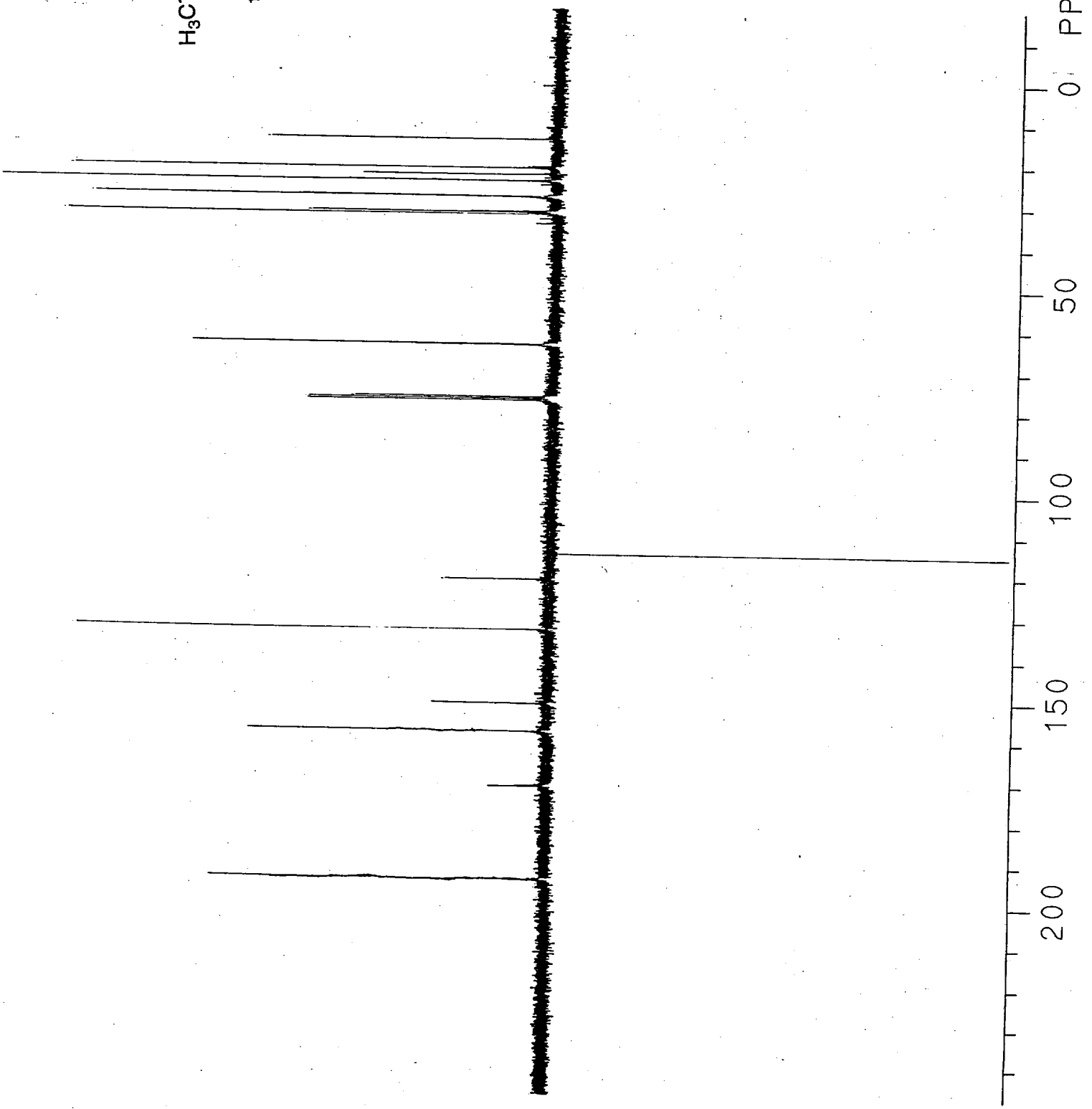
Compound 16

^{1}H NMR, $CDCl_3$, 300 MHz



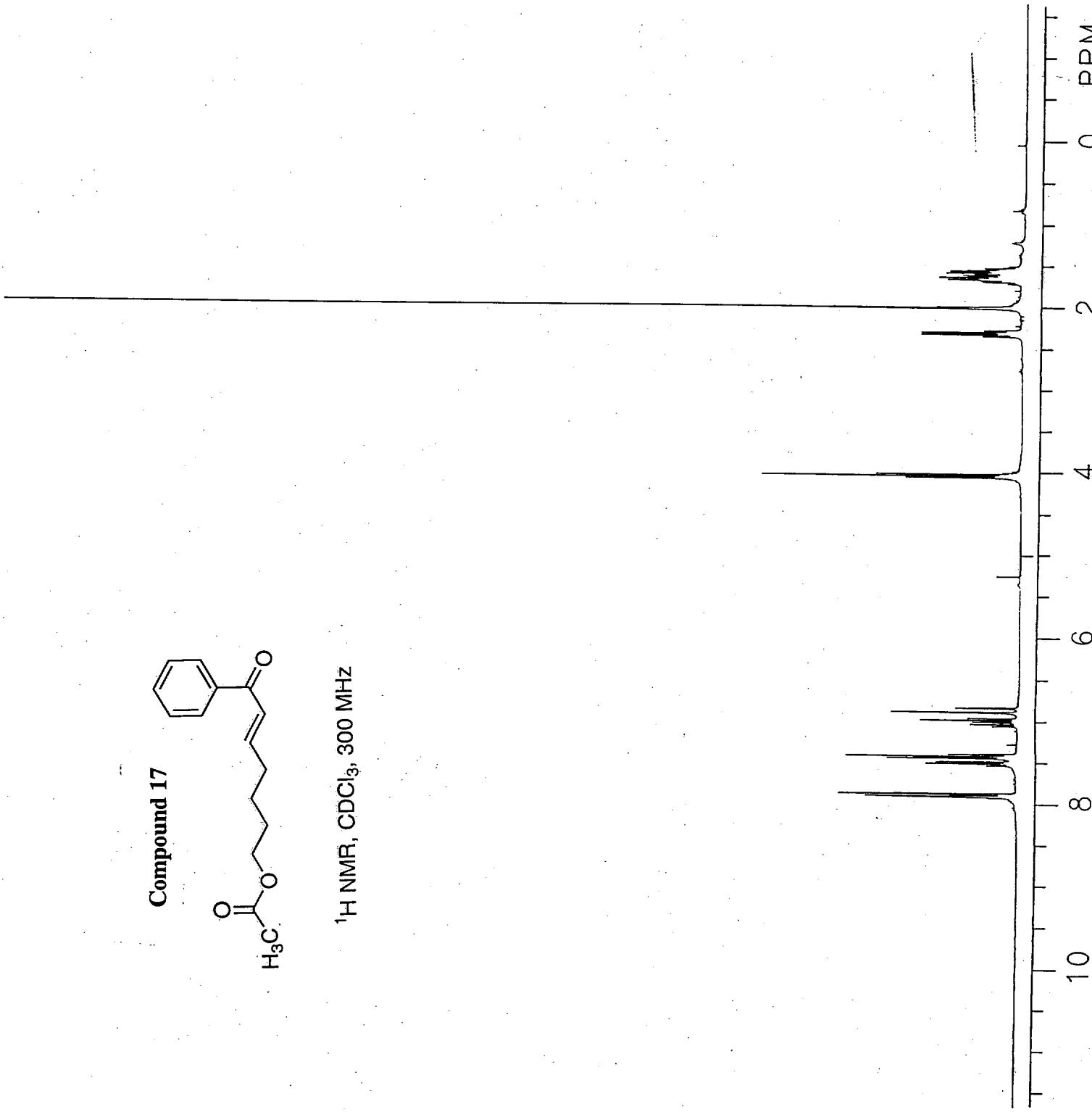
Compound 16

^{13}C NMR, $CDCl_3$, 75 MHz

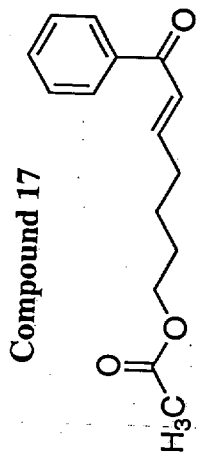


Compound 17

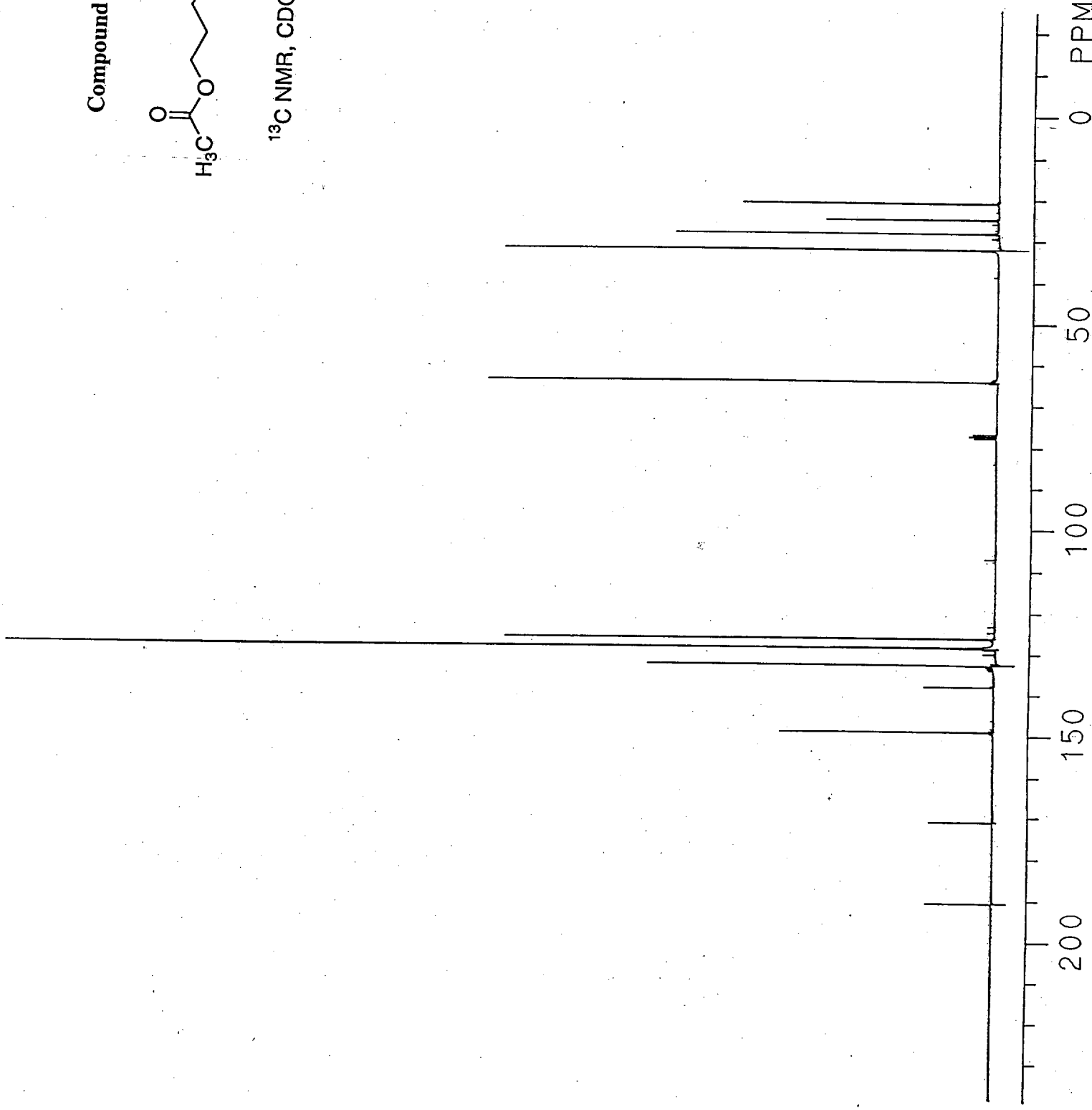
^{1}H NMR, $CDCl_3$, 300 MHz



Compound 17



^{13}C NMR, $CDCl_3$, 75 MHz



Compound 18

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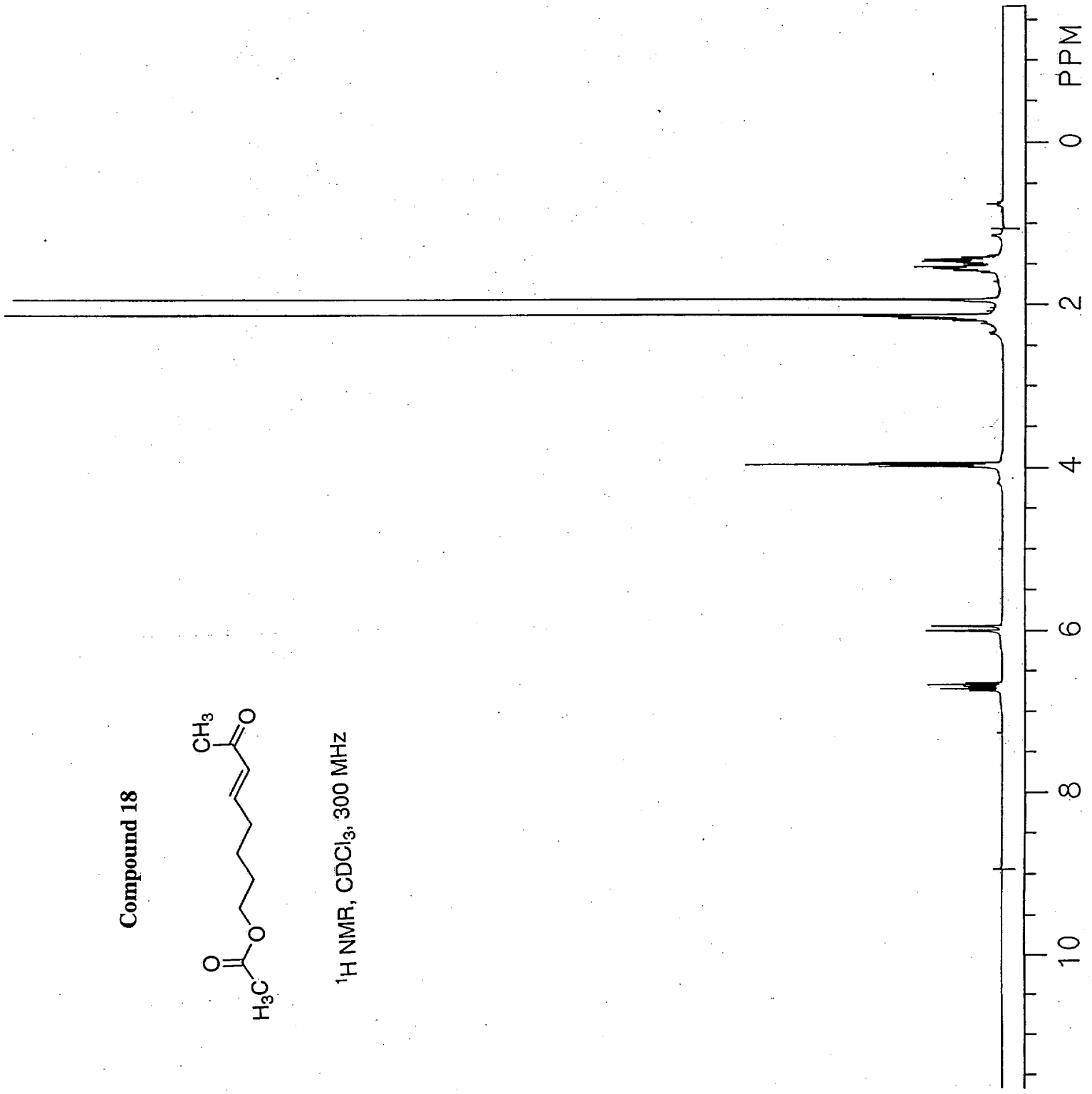
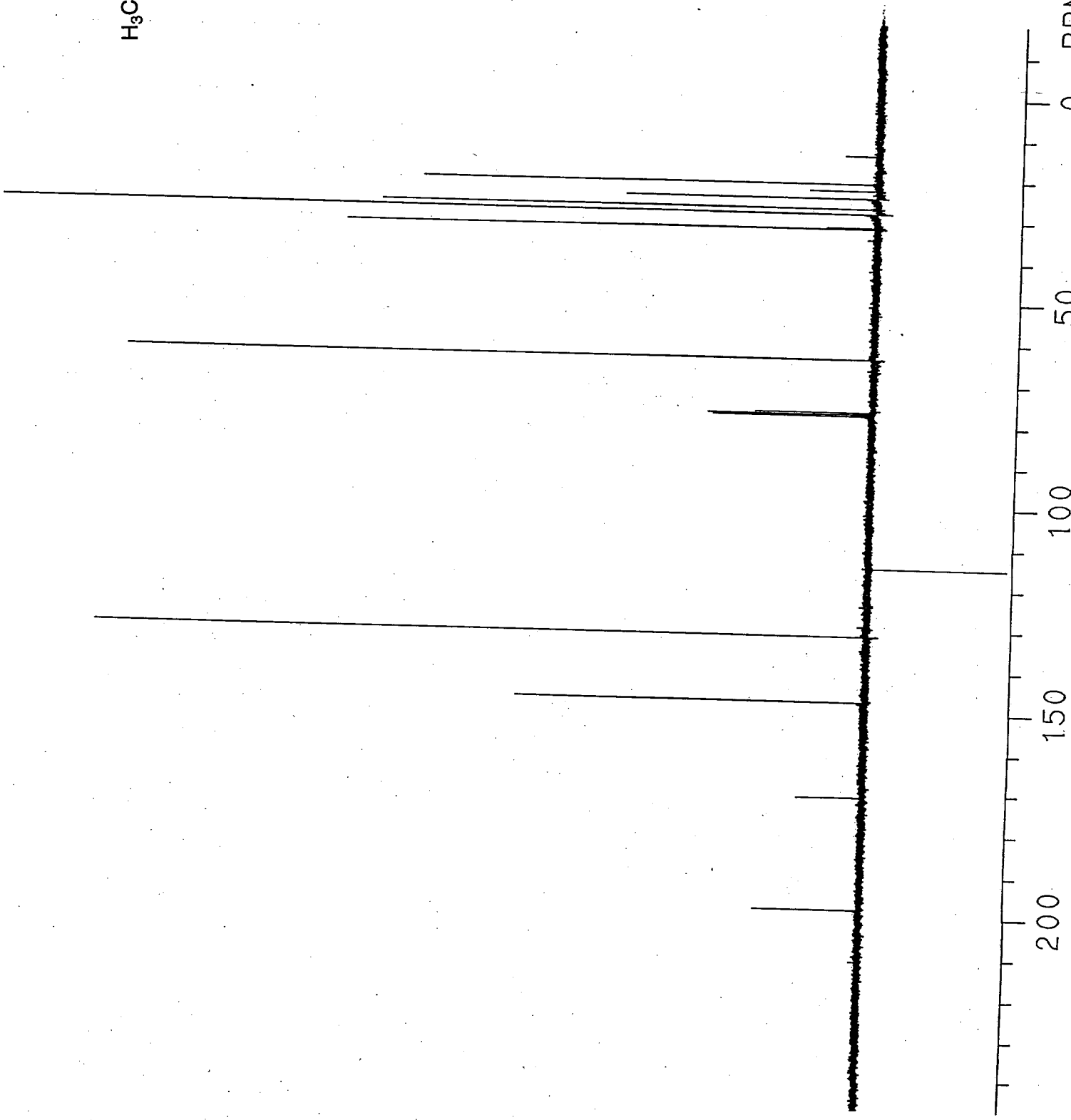
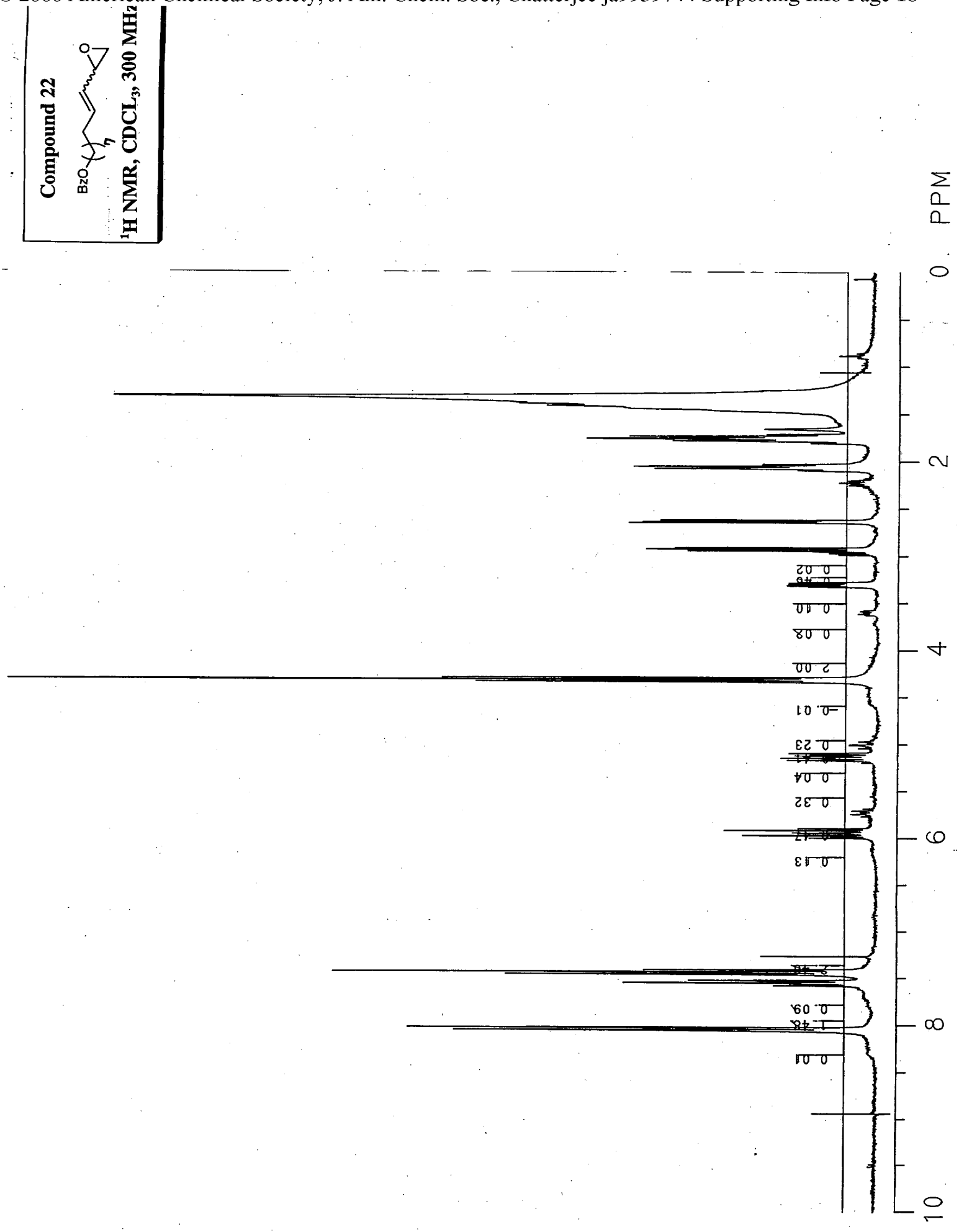


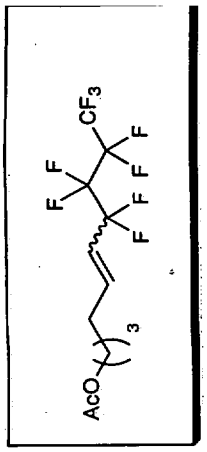
Compound 18

^{13}C NMR, $CDCl_3$, 75 MHz

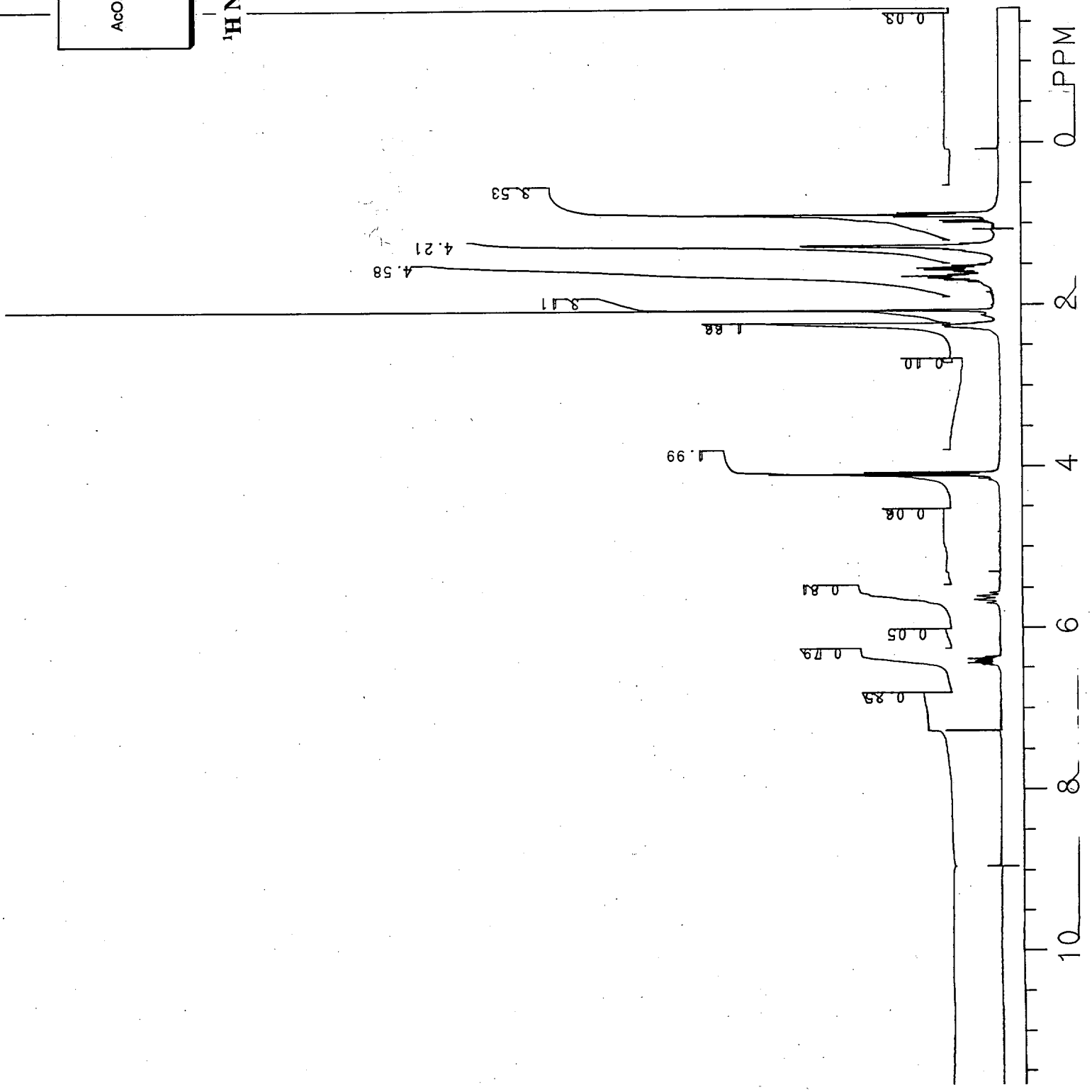




Compound 23



^{1}H NMR, $CDCL_3$, 300 MHz



Compound 24

^{1}H NMR, $CDCL_3$, 300 MHz